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(54) Resin encapsulated semiconductor devices

(57) An organic polymer film, e.g. aromatic polyimide resin 6, having a moisture permeability of 1×10^{-7}g.cm/cm².hr or less is formed between the encapsulating resin 8 of a semiconductor device, and a moisture absorption member 2, 3, 4 such as a phosphosilicate glass or SiO_2 film, a hygroscopic polyimide film or a corrodible aluminium wiring conductor. The low moisture permeability film is formed on the surface of the semiconductor device either directly or through the medium of other material, and may serve as a protective or possivation film, an α-ray shield or an inter-layer insulating film. Methods for the production of the low moisture permeability film are described, and the use of fillers such as silica or alumina is disclosed.

FIG. 1

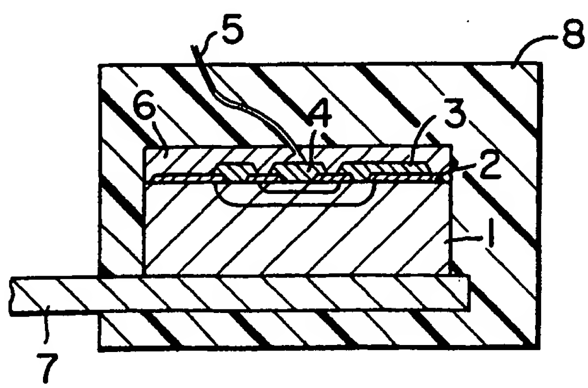

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FIG. 1

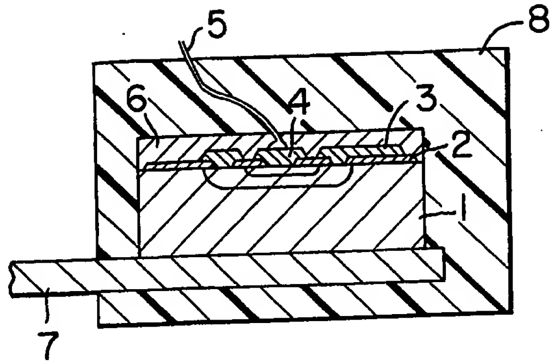


FIG. 2

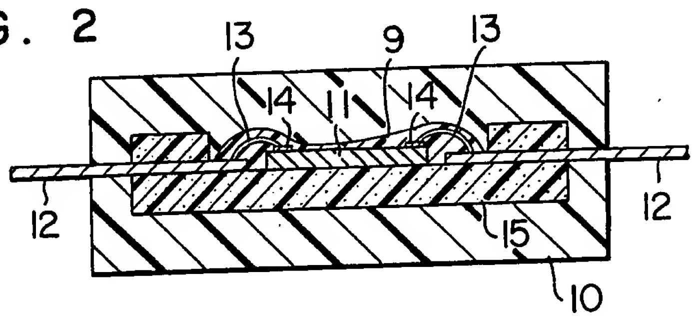


FIG. 3

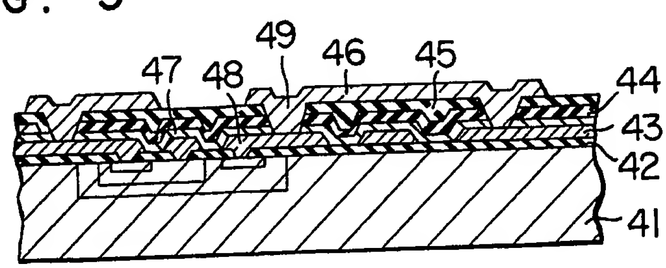


FIG. 4

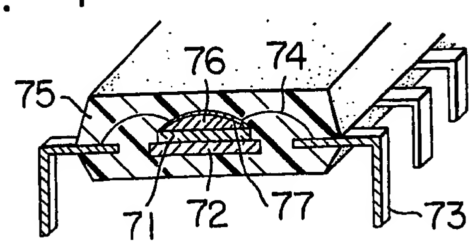
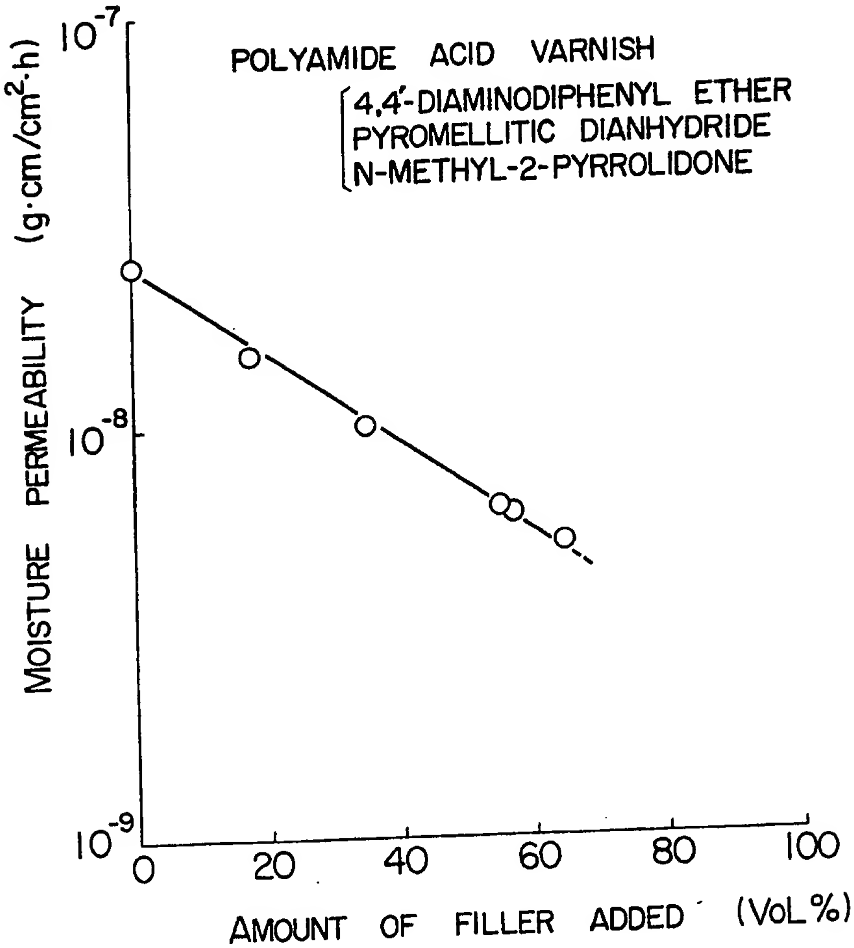


FIG. 5


POLYAMIDE ACID VARNISH
4,4'-DIAMINODIPHENYL ETHER
PYROMELLITIC DIANHYDRIDE
N-METHYL-2-PYRROLIDONE
MOISTURE PERMEABILITY (g·cm/cm²·h)
10⁻⁷
10⁻⁸
10⁻⁹
0
20
40
60
80
100
AMOUNT OF FILLER ADDED (VoL%)

SPECIFICATION

Resin encapsulated semiconductor devices

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to resin encapsulated semiconductor devices, and more particularly it relates to the improvement in the semiconductor device obtained by molding with a packaging resin a semiconductor element having an organic polymer coating film of low moisture permeability, such as a polyimide resin film, which is useful as a material for passivation, PSG film protection, α-ray shielding, insulation of multilevel metal layers, etc.

DESCRIPTION OF THE PRIOR ART

Exposed surfaces of p–n junction formed on semiconductor substrates are usually coated with various types of passivating materials since such exposed surfaces are highly susceptible to influences from the ambient environment. Japanese Patent Appln Kokai (Laid-Open) No. 8469/75 discloses a passivation technique using a polyimide resin, which has an advantage of allowing prosecution of the passivation treatment at low temperatures, in place of conventional inorganic passivation materials such as silicon dioxide, silicon nitride, alumina and glass. The polyimide resin disclosed in this patent specification is one (polyimide-isoindolo-quinazolinedion resin) obtained from pyromellitic acid dianhydride, benzophenonetetracarboxylic acid dianhydride, diaminodiphenyl ether and diaminodiphenyl ether mono-carbonamide, and it is stated in said patent specification that the semiconductor substrate and the like is pretreated with an aminosilane coupling agent for bettering adhesion between said polyimide resin and semiconductor substrate.

Japanese Patent Appln Kokai (Laid-Open) Nos. 6279/75 and 6280/75 discloses resin encapsulated semiconductor devices and teach techniques for minimizing troubles of semiconductor integrated circuit devices due to penetration of moisture from the outer atmosphere by covering interfaces between the encapsulating (or packaging) resin and lead frames, semiconductor integrated circuit chips and lead wires with a polyimide resin. U.S. Patent No. 4,079,511 also discloses a semiconductor device coated with an encapsulation material to prevent moisture from reaching integrated circuit chips.

Further, U.S. Patent Nos. 4,001,870, 4,017,886, 4,040,083 and 4,060,828 disclose techniques using polyimide resins as an insulating film material for multi-level metal layers, and U.S. Patent No. 4,040,083 proposes a pretreatment of semiconductor chips with an aluminium chelate compound for improving adhesion between polyimide resin and SiO_2 film.

Use of phosphosilicate glass (hereinafter referred to as "PSG"), which is capable of keeping off sodium ions and the like, for the protection film is also a known means for improving moisture resistance of semiconductor devices.

This PSG is produced by mixing gases serving as the Si source and P source, such as a silane and a phosphine, and oxidizing and depositing them on an element by a CVD (chemical vapor deposition) method. Its ion inhibitory performance can be elevated by increasing the phosphorus concentration in the mixture. Also, the deposited film can be made into a flowable film by subjecting such film to a heat treatment (after-treatment).As the film is made flowable, the film corners are rounded and also the level difference on wiring plane is reduced to make the wiring more durable and less liable to break. It also makes possible wire bonding at the active areas of the element.

However, the increase of phosphorus concentration results in a greater tendency of PSG to elute in water, and when the phosphorus concentration reaches 10 and odd percents by mole, PSG comes to show deliquescence. Therefore, the moisture resistance becomes more important for PSG with higher phosphorus concentration, and it becomes a serious problem in case the phosphorus concentration exceeds 10% by mole at which the glass becomes flowable.

On the other hand, in the field of semiconductor memory devices, techniques are known to form an α-ray shielding layer on the circuit side of the semiconductor memory element for preventing soft errors originating in the α-rays emitted from radioactive elements uranium and thorium in the encapsulating material in the semi-conductor memory device of high integration performance, and there has been proposed a resin encapsulated semi-conductor memory device using as said shielding material a polyimide resin with extremely reduced contents of uranium and thorium.

It is recognized that the greatest problem with these known resin encapsulated semiconductor devices (as compared with ceramic or glass encapsulated semi-conductor devices) lies in poor moisture resistance because the resin itself is permeable to water and also the gaps are formed between the resin and the semiconductor substrate and between the resin and the metal wires to admit moisture penetration. For alleviating such problem, it is generally practiced to treat the interfaces between undercoat resin and semiconductor chips and between PSG protecting film

and metal wires with a coupling agent or such.

It is known that, in general, the resin material use in the field of semiconductor devices is required to have high moisture resistance. For example silicone resin, which is per se moisture resistant and water repellent, is widely used as passivation material. However, because of high moisture permeability, silicone resins can hardly prevent intrusion of moisture from the outer atmosphere into the highly hygroscopic material such as SiO_2 film, PSG film and/or polyimide series polymer film formed on the semiconductor element.

Various types of polyimide resins, especially afore-mentioned polyimide-isoindoloquinazolinedion resin, have come to be used widely in the field of integrated circuits owing to their many excellent properties such as heat resistance, insulating characteristics, film-forming properties, workability, etc., in addition to their strong adhesiveness to the semiconductor chips and metal films.

However, as a result of studies on the semi-conductor devices using various types of polyimide resins including said polyimide-isindoloquinazolinedion resin, the present inventors found that some of such semiconductor devices break down or develop some sort of trouble in the course of severe long-time moisture resistance test. In search of the causes thereof, the present inventors have examined moisture resistance of encapsulating resins, adhesiveness of encapsulating resins to the undercoat or polyimide resin film formed as a stabilized film, adhesion between the polyimide resin film and the semiconductor chips, PSG protective film, metal wires, etc., and found that a primary case of the trouble is moisture permeability of the polyimide resin itself. It has been generally conceived that if a polyimide resin film is fastly attached to a semiconductor chip or metal wire, no moisture is allowed to penetrate therethrough. However, the fact that there could arise a trouble or breakdown due to moisture even if the semiconductor chips are pretreated with a coupling agent has made us convinced that the problem cannot be solved by merely improving adhesion between the semiconductor element and the polyimide resin. All the facts indicate that said trouble or breakdown is attributed to moisture permeability of the polyimide resin.

SUMMARY OF THE INVENTION

The present invention provides a resin encapsulated semiconductor device having a passivation film, an insulating film of multilevel metal layers or an α-ray shielding layer which has been remarkably improved in moisture resistance, particularly in moisture permeability. The present invention especially provides a resin encapsulated semiconductor device of the type in which a SiO_2 film, PSG protective film or other organic polymer film such as polyimide-isoindoloquinazolinedion resin film with high hygroscopicity is formed on p-n junctions or aluminium wiring of the semiconductor element, characterized in that said highly hygroscopic material is overcoated with a polymer film of low moisture permeability so as to inhibit the moisture in the outer atmosphere from reaching said material or to prevent the access of moisture thereto.

According to an embodiment of this invention, there is provided a semiconductor device comprising a semiconductor substrate, an insulating film formed on said substrate, a function element having a metal conductor formed on said insulating film and a PSG protective layer and polyimide resin film formed in contact with said conductor, an encapsulating resin packaging said function element to give a mechanical protection thereto, and at least one external lead extending from said encapsulating resin, wherein said polyimide resin is an aromatic polyimide resin having a moisture permeability of 1×10^{-7} g.cm/cm².h or below.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a sectional view showing the construction of a resin encapsulated semiconductor device according to this invention.

Figure 2 is a sectional view showing the construction of another resin encapsulated semiconductor device in which the present invention is adopted.

Figure 3 is a sectional view showing the construction of a resin encapsulated semiconductor device having a multi-layer wiring assembly adopted with the present invention.

Figure 4 is a perspective view, partly shown in section, illustrating the construction of a resin encapsulated memory according to this invention.

Figure 5 is a diagram for better understanding of an embodiment of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention is now described in detail with reference to the accompanying drawings.

In Fig. 1, reference numeral 1 indicates a semiconductor substrate such as a silicon substrate having, for example, p-n-p type transistors formed in its surface layer. On the surface of said semiconductor substrate 1 is formed a silicon dioxide film 2 provided for the purpose of insulation and passivation among the emitter, base and collector. Also, a base electrode 3 and an emitter electrode 4 are formed by aluminium deposition film. When packaging these planar transistors, the substrate 1 is secured to an end of a tab lead 7, and the other electrode of the

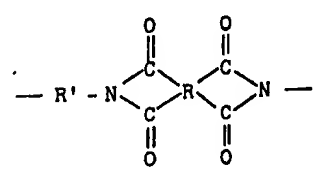
element and the lead wire are wire bonded by a gold or aluminium wire 5. After coated and protected with an undercoat resin 6, the semiconductor substrate 1 including the end of the tab lead 7 is molded with a resin 8 for providing mechanical strength and protecting the substrate from the outer air.

Fig. 2 shows a semiconductor device having its integrated circuit encapsulated with a resin. The semiconductor integrated circuit 11 is fixed in position on a package 15 made of ceramic or other material, and the bonding pads 14 provided at the periphery of the integrated circuit block 11 and the external lead terminals 12 of the package are connected by a fine metal wire 13. Also, an undercoat film 9 formed form a moisture resistant polyimide resin is provided so as to cover generally said integrated circuit block 11, fine metal wires 13, lead terminal 12 and bonding pads 14 connected by the metal wires 13, and the entire package is encapsulated with a molding resin 10. This invention can be also applied to thick-film circuits.

Fig. 3 shows an embodiment of resin encapsulated semiconductor device having a two-layer wiring assembly on the semiconductor substrate surface. A metal coating is formed on the semiconductor substrate 41 having a silicon dioxide film 42 and the metal at the unnecessary parts is removed by a conventional etching technique to form a first conductor layer 43 having a desired wiring pattern. This conductor layer 43 is electrically connected to the semiconductor element through-holes 48 provided at the specified locations in the silicon dioxide film 42. Then a silicon dioxide film 47 is coated on the layers, 42, 43 by a known method such as chemical vapor phase growing method or high frequency sputtering, and then through-holes are formed in said silicon dioxide film at the parts necessary for connection to the conductor. On said silicon dioxide film 47 is formed an aminosiliane compound film 44, on which is formed a polyimide resin film 45. The required parts of this polyimide resin film are etched out to partly expose the first conductor layer 43, and a second conductor layer 46 is formed thereon. In this example, the insulating layer has a double layer structure consisting of the silicon dioxide layer 47 and the polyimide resin layer 45.

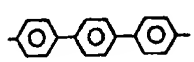
Fig. 4 shows a sectional view of a dual-in-line type resin packaged semiconductor memory device having an α-ray shielding layer between the semiconductor memory element and its resin package. In Fig. 4, reference numeral 71 indicates a semicondctor memory element made from silicon chips and secured to an silicon chip support 72. Numeral 73 denotes leads connected to the electrode pads of the memory element 71 by bonding wires 74. Numeral 75 indicates an encapsulating resin and 76 shows an α-ray shielding layer. In this embodiment, the α-ray shielding layer 76 is applied on the surface of the memory element and dry-hardened, and an overcoat 77 of low moisture permeability is formed on said shielding layer to inihibit moisture penetration.The encapsulation resin block 75 is molded with a thermosetting resin such as epoxy resin.

The semiconductors are required to have moisture resistance sufficient to stand a 1,000-hour test under the conditions of 80°C and 90% RH. The polyimide resins which have passed this test were all those having a moisture permeability of 1×10^{-7} g. cm/cm²·h or below at 25°C/75% RH. Among such polyimide resins is preferably used on having the structural units represented by the following general formula:

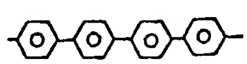


(I)

wherein R is an aliphatic or aromatic group, and R′ is an aromatic group. It has been found that when R′ contains therein



and/or



the resulting polyimide films showed very small moisture permeability.

According to this invention, a coating film of a specific polyimide resin selected from those represented by the above-shown general formula (I) is provided on the water-corrodible aluminum wiring conductor or water-elutable PSG protective layer to improve moisture resistance of said aluminium wiring or PSG protective layer to provide a resin encapsulated

semiconductor device with excellent characteristics (reduced rate of failure with the lapse of time). There is also provided an excellent semiconductor element having p–n junctions which is proof against property deterioration by moisture in the outer air by covering the semiconductor surface having exposed p–n junctions with said polyimide resin coating film.

The thickness of said coating film according to this invention is selected to be within the range of 1–300 μm, and then the element is molded with a molding material. The thickness of the molding resin is usually selected to be within the range of about 0.5–5 mm.

A problem is pointed out that soft errors could be caused when α-rays enter the semiconductor memory element having a high integration capacity. The main sources of these α-rays are uranium and thorium which are contained in very small quantities in the encapsulating material such as ceramic, metal or molding resin. Therefore, the above problem is solved if such uranium and thorium are eliminated from the encapsulating material. It is attempted to minimize the uranium and thorium contents by refining the encapsulating material.

Many attempts have also been made for shielding α-rays by a protective coating film. In case the semi-conductor device is a memory, it is possible to prevent the soft error due to α-rays by selecting the thickness of the polyimide resin film of this invention so that it is 35 μm or above. In this case, if the protective coating film is refined so that the uranium and thorium contents therein becomes less than 0.1 ppb as in the case of the encapsulating material, generation of α-rays from the polyimide resin itself practically offers no problem. Such refining can be conveniently accomplished by means of distillation, sublimation, recrystallization or extraction of the monomer or solvent. In order to minimize corrosion or less in the moisture resistance test, refining is also required to reduce the sodium content to less than 1 ppm, and such refining can be accomplished in the same way as said above.

The polyimide resins represented by the above-shown general formula (I) or their precursor polyamide acid resins used in this invention can be obtained from an equimolar reaction of an aromatic diamine and an aromatic tetracarboxylic acid dianhydride by using, for example, a solution polycondensation method.

The reaction solvent used in the solution polymerization needs to be one which is capable of dissolving both of the aromatic diamine and aromatic tetracarboxylic acid dianhydride. Examples of such reaction solvents usable in this invention are N,N-dimethylformamide, NN-diethylformamide, dimethyl sulfoxide, N,N-dimethylacetamide, N,N-diethylacetamide and N-methyl-2-pyrrolidone. These reaction solvents may be used in admixture of two or more of them if necessary for certain purposes such as facilitating the dissolving operation.

As the examples of the aromatic tetracarboxylic acid dianhydrides usable in this invention, the following may be cited, pyromellitic acid dianhydride (PMDA), benzophenonetetracarboxylic acid dianhydride (BTDA), 1,4,5,8-naphthalenetetracarboxylic acid dianhydride, 2,3,6,7-naphthalenetetracarboxylic acid dianhydride, 1,2,5,6-naphthalenetetracarboxylic acid dianhydride, 3,3',4,4'-diphenyltetracarboxylic acid dianhydride, 2,2',-3,3'-diphenyletracarboxylic acid dianhydride, 2,3,3',4'-diphenyltetracarboxylic acid dianhydride, 2,2-bis(3,4-di-carbophenyl)propane dianhydride, 2,2-bis[4-(3,4-dicarboxy-phenoxy)phenyl]propane dianhydride, 2,2-bis[4-(2,3-dicarboxy-phenoxy)phenyl]propane dianhydride, bis(3,4- dicarboxyphenyl)sulfone dianhydride, bis(3,4-dicarboxy-phenyl)ether dianhydride, bis(3,4-dicarboyphenyl)methane dianhydride, perylene-3,4,9,10-tetracarboxylic acid dianhydride and mixtures thereof.

As for the aromatic diamines used in this invention, 4, 4'''-diamino-p-terphenyl and 4,4''-diamino-quaterphenyl are useful for achieving the effect of this invention.

It is also possible to use the polyimide resins synthesized from copolycondensation polymerization of said various types of acid dianhydiirdes by using the other generally known diamines, such as cited below, in a defined range where the moisture permeability stays below 1×10^{-7} g·cm/cm^2·h and also the effect of this invention won't be impaired. Examples of said diamines are p-phenylenediamine, m-phenylenediamine, 4,4'-diamino-diphenyether, 4,4'-diaminodiphenylmethane, 4,4'-diamino-diphenylsulfone, 4, 4'-diaminodiphenylpropane, 4, 4'-diaminodiphenylsulfoxide, 1,5-diaminonaphthalene, 4,4'-diaminodiphenylethane, m-toluylenediamine, p-toluylene-diamine, 3,4'-diaminobenzanilide, 1,4-diaminonaphthalene, 3,3'-dichloro-4,4'-diaminodiphenyl, 4,4'-diaminodiphenyl-amine, 4,4'-diaminodiphenyl-N-methylamine, 4,4'-diamino-diphenyl-N-phenylamine and 3,3'-diaminodiphenylsulfone.

The present inventors confirmed that the object of this invention can well be achieved by mixing in the polyimide resin of this invention other polymers having a moisture permeability below 1×10^{-7} g·cm/cm^2·h in an amount within the range where the object and effect of this invention won't be impaired. Examples of such pólymers are fluorine resins such as ethylene tetrafluoride polymers, ethylene tetrafluoride-propylene hexafluoride copolymers and polyvinylidene fluoride.

It was also found that addition of a finely powdery filler such as silica or alumina to an ordinary polyimide resin having a moisture permeability above 1×10^{-7} g·cm/cm^2·h results in a considerable reduction of moisture permeability, and this method proves effective for lowering the failure rate of the semiconductors.

These fillers can not be used in a merely pulverized form without refining because such fillers contain too much impurities for use in the semiconductor memory elements. Therefore, these fillers, when used as a coating material for the semiconductor memory elements, need be refined in the following way to such an extent that generation of α-rays, which is a cause of soft errors, is restrained to a practically negligible degree. Refining is performed by distilling, for example, a silicon or aluminium compound having hydrolyzable groups bonded to silicon or aluminium, then subjecting said compound to hydrolysis and cohydrolysis, and then heating and oxidizing it.

It is to be noted that the coating material added with said filler involves a problem that the coating film properties might be impaired when the particle size or the amount of the filler added is increased, so that in use of such coating material for the semiconductor elements it is necessary to select a composition within the proper range.

The polyimide of this invention is coated on the surface of an element in the form of a polyamide acid varnish synthesized in said reaction solvent and then heated at around 100–450°C for several hours to form a polyimide coating film, and thereafter the thus treated element is molded with a molding material such as epoxy resin, phenol resin, diallyl phthalate resin, unsaturated polyester resin, silicone resin or the like to a thickness of about 0.5–5 mm by using such techniques as casting, transfer molding, injection molding, etc.

The thus formed polyimide film can serve as a protective film or an inter-layer insulating film for the corrodible aluminium wiring conductors, PSG protective layers and semiconductor surfaces at p–n junctions.

It will be appreciated that polyimide coating according to this invention provides a semiconductor device with excellent moisture resistance as compared with the semic onductor devices provided with conventional polyimide protective coat.

The present invention is further described hereinbelow by way of the embodiments thereof, but the invention is not limited in any way by these examples.

In all of the embodiments described hereinbelow, a pretreatment was performed with an aminosilane compound prior to polyimide coating.

Example 1

0.1 Mole of 4,4''-diamino-p-terphenyl and 0.1 mole of pyromellitic acid dianhydride (hereinafter referred to as "PMDA") were reacted in N-methyl-2-pyrrolidone (hereinafter referred to as "NMP") at 20–30°C to obtain a varnish having about 15% of involatiles and uranium and thorium contents below 0.1 ppb.

This varnish was coated on a MOS type 16k-bit RAM element and heated at 100°C for one hour, at 200°C for 2 hours and at 250°C for 3 hours to form a polyimide film with a thickness of about 50 μm on the element surface, followed by transfer molding with an epoxy resin to obtain a semiconductor device.

The failure rate of this semiconductor device after standing under the conditions of 80°C and 90% RH for a period of 1,000 hours was as low as 0/120.

Also, the soft error rate of this memory was below 100 fits (one fit is a unit signifying occurence of one error per 10^9 hours per element).

The moisture permeability of said polyimide film under the conditions of 25°C and 75% RH was 1.8×10^{-8} g·cm/cm²·h.

Comparative Example 1

0.1 Mole of 4,4'-bis(p-aminophenoxy)biphenyl and 0.1 mole of PMDA were reacted in NMP at about 10°C to obtain a varnish with an involatile content of 15% and uranium and thorium contents of less than 0.1 ppb.

This varnish was coated on the surface of an element, followed by resin encapsulation in the same way as Example 1 to obtain a semiconductor device. The failure rate of this semiconductor device as measured under the same conditions as in Example 1 was 12/56. The soft error rate of this memory also measured in the same way as Example 1 was below 100 fits, and the moisture permeability of this polyimide film under the conditions of 25°C and 75% RH was 4.5×10^{-7} g·cm/cm²·h.

Example 2

0.05 Mole of 4,4'''-diamino-quaterphenyl, 0.05 mole of 4,4'-diaminodiphenyl ether and 0.1 mole of benzophenonetetracarboxylic acid dianhydride (hereinafter referred to as "BTDA") were reacted in NMP at about 10°C to obtain a varnish containing about 15% of involatiles, and this varnish was applied to a resin encapsulated diode as described below.

Sais varnish was coated along the p–n junction on the side of a semiconductor element and then heated and dried at 100°C for one hour, at 200°C for 2 hours and at 250°C for 3 hours to form a polyimide film, and the thus coated element was molded with an epoxy resin to obtain a semiconductor device. Its failure rate after standing under the conditions of 80°C and 90% RH

for a period of 1,000 hours was 0/80, and the moisture permeability of this polyimide film at 25°C/75% RH was 3.5×10^{-8} g·cm/cm²·h.

Comparative Example 2

0.1 Mole of 4,4'-diaminodiphenyl ether and 0.1 mole of BTDA were reacted in NMP at about 10°C to obtain a varnish with about 15% of involatile component, and by using this varnish, a resin encapsulated diode was obtained in the similar way to Example 2 and tested under the same conditions as in Example 2. Its failure rate was 84/240, and the moisture permeability of the polyimide film under the conditions of 25°C and 75% RH was 2.5×10^{-7} g.cm/cm²·h.

Example 3

0.1 Mole of 4,4"diamino-p-terphenyl, 0.05 mole of PMDA and 0.05 mole of BRDA were reacted in NMP at 20–30°C to obtain a varnish with about 15% of involatile component.

A 5,500 Å thick thermal oxidation film (SiO_2) was formed on the surface of a silicon substrate, and after vacuum depositing a 1 μm thick aluminium film on said surface, a first wiring conductor layer was formed according to the conventional process. Then above-said varnish was spin coated thereon and heated at 100°C for one hour, at 200°C for another one hour and at 250°C for 2 hours to form an approximately 2 μm thick polyimide resin layer insulating film. After forming through-holes, second layer aluminium wiring was worked and then a protective layer (5,500 Å thick) of PSG (prepared by the CVD method) with 12% by mole phosphorus concentration was formed thereon. After bonding, said varnish was coated and baked to form a 35 μm thick polyimide protective film, and then this element was transfer molded with an epoxy resin to obtain a semiconductor device.

This semiconductor device, when left in an atmosphere of 80°C and 90% RH, showed no sign of abnormality even after the lapse of 1,000 hours.

The moisture permeability of this polyimide film under the conditions of 25°C and 75% RH was 1.6×10^{-8} g.cm/cm²·h.

Comparative Example 3

0.1 Mole of 4,4'-diaminodiphenylmethane, 0.05 mole of PMDA and 0.05 mole of BTDA were reacted in NMP at about 10°C to obtain a varnish with about 15% of involatile component, and the same test as in Example 3 was conducted by using this varnish. As abnormality was observed upon passage of 800 hours, the defective parts were dismantled and examined. It was found that the aluminium wiring of the element had been corroded all over in both first and second layers.

The moisture permeability of this polyimide film at 25°C and 75% RH was 4×10^{-7} g.cm/cm²·h.

Example 4

0.1 Mole of 4,4"-diamino-p-terphenyl, 0.08 mole of PMDA and 0.02 mole of BTDA were reacted in NMP at 20–30°C to obtain a varnish with about 15°C of involatiles.

This varnish was coated on an LSI having a protective layer of PSG (CVD method) with 10% by mole phosphorus concentration and heated at 100°C for one hour, at 200°C for another one hour and at 300°C for additional one hour to form an approximately 50μm thick protective film. This element was then molded with an epoxy resin to obtain a semiconductor device.

The failure rate of this device after standing at 80°C and 90% RH for a period of 1,000 hours was 0/150, and the moisture permeability of the polyimide film at 25°C and 75% RH was 1.5×10^{-8} g·cm/cm²·h.

Comparative Example 4

A varnish with about 15% of involatile component was obtained by reacting 0.1 mole of 4,4'-diaminodiphenylmethane, 0.08 mole of PMDA and 0.02 mole of BTDA in NMP at about 10°C, and by using this varnish, a semiconductor device was produced in the same way as Example 4 and subjected to the moisture resistance test under the same conditions as in Example 4. Its failure rate was 42/56 and the moisture permeability of the polyimide film at 25°C and 75% RH was 3.6×10^{-7} g·cm/cm².h.

Example 5–8

The polyamide acid varnish obtained in Example 1 and the polyamide acid varnish obtained in Comparative Example 1 were mixed in ratios shown in the following table to prepare four specimens of mixed polyamide acid varnish, and by using these varnish specimens, the resin molded RAM's were produced after the manner of Example 1 and subjected to the same moisture resistance test as conducted in Example 1.

	Polyamide acid varnish of Example 1	:	Polyamide acid varnish of Comparative Example 1	Failure rate after 1,000 hours at 80°C and 90% RH	Moisture permeability at 25°C and 75% RH (g.cm/cm².h)
Example 5	80	:	20	0/95	3.5×10^{-8}
Example 6	60	:	40	0/89	6.5×10^{-8}
Example 7	40	:	60	2/93	1.3×10^{-7}
Example 8	20	:	80	9/96	2.5×10^{-7}

Example 9

0.1 Mole of 4,4″-diamino-p-terphenyl and 0.1 mole of BTDA were reacted in NMP at 20–30°C to obtain a varnish with about 15% of involatile component, and this polyamide acid varnish was added with 10% by weight of pulverized ethylene tetrafluoride resin with an average particle size of 0.1–50μm. The thus prepared varnish was applied on an LSI having a protective layer of PSG (CVD method) with 10% by mole phosphorus concentration and heated at 100°C for one hour, at 200°C for 2 hours and at 400°C for additional 2 hours to form an about 50μm thick protective film, followed by molding with an epoxy resin to obtain a semicondctor device.

No abnormality was observed after standing in an atmosphere of 80°C and 90% RH for a period of 1,000 hours.

This semiconductor device was further subjected to a pressure cooker test by leaving the semiconductor device in a saturated steam atmosphere of 120°C and 2 atm. No abnormaility was admitted even after the lapse of 120 hours.

The moisture permeability of this fluorine resin-containing coating film at 25°C and 75% RH was 1.3×10^{-8} g.cm/cm²·h.

Example 10

Refined high-purity silica powder was added as filler to the polyamide acid varnish obtained in Comparative Example 3, and its moisture permeability was measured. As a result, it was found that the moisture permeability lowers as the amount of filler added increases as shown in Fig. 5, and when the amount of filler added exceeds 35% by volume, the moisture permeability of the film according to this invention becomes lower than 1×10^{-8} g.cm/cm²·h. When the amount of filler added was over 70% by volume, the coating properties were excessively deteriorated and no uniform coating could be made on the semiconductor element.

Said varnish added with 50% by volume of said filler was then applied on an LSI element and heated at 100°C for one hour and at 200°C for 5 hours to form a 70 μm thick protective film, and then this element was transfer-molded with an epoxy resin to obtain a semiconductor device. Its failure rate after standing at 80°C and 90% RH for a period of 1,000 hours was 0/180.

Example 11

Described in this Example is the case where the varnish obtained in Example 1 was used for forming an inter-layer insulating film for multi-layer wiring of LSI.

Aluminium was vacuum deposited to a thickness of 2μm on the surface of a silicon substrate having a thermal oxidation film of SiO_2, and then a first wiring conductor layer was formed according to a conventional method. Then the polyamide acid varnish obtained in Example 1 was spin coated thereon and then heated and hardened to form a 4μm thick polyimide film. After forming through-holes, a second aluminium wiring conductor layer was formed. Said varnish was further applied thereon and heated and hardened to form a 4 μm thick polyimide film, and then this polyimide film was selectively etched by using a photoresist to form through-holes. Thereafter, a third aluminium wiring conductor layer was formed. After bonding, said varnish was coated thereon as a wiring protective film and heated and hardened to form a 45 μm thick polyimide film.

This element was then encapsulated with an epoxy resin and subjected to the standing test in an atmosphere of 80°C and 90% RH. Its failure rate after passage of 1,000 hours was 0/40.

As described above, this invention can offer the semiconductor devices with excellent moisture resistance by providing a specific polyimide protective film or inter-layer insulating film on the aluminium wiring conductors and semiconductor surfaces with exposed p–n junctions or on the CVD method PSG protective layer.

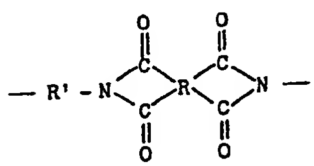
CLAIMS

1. A resin encapsulated semiconductor device made by encapsulating a semiconductor element with a resin characterized in that an organic polymer film having a moisture permeability of 1×10^{-7} g.cm/cm^2·h or below is provided on the surface of said semiconductor element either directly or through other insulating material.

2. A resin encapsulated semiconductor device according to Claim 1, wherein said organic polymer film is formed on a passivation film formed on the end face of the p–n junction exposed in the surface of the semiconductor element.

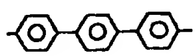
3. A resin encapsulated semiconductor device according to either of Claims 1 and 2, comprising a semiconductor element and a conductor layer formed thereon with an insulator layer placed therebetween, wherein the saturated moisture absorption rate of said insulator layer at 25°C and 70% RH is 1% or above and said organic polymer film is formed on said insulator layer.

4. A semiconductor device according to any one of Claims 1 to 3, wherein the organic polymer film is made from a polyamide resin having the following recurring unit:

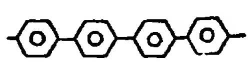


wherein R is an aliphatic or aromatic group, and R′ is an aromatic group.

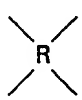
5. A resin encapsulated semiconductor device according to Claim 4, wherein -R′- in the formula (I) contains



and or

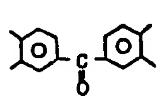


6. A resin encapsulated semiconductor device according to Claim 4, wherein



in the formula (I) is

and or



7. A resin encapsulated semiconductor device according to any one of Claims 4 to 6, wherein the polyamide resin film has a thickness of 1–300μm.

8. A resin encapsulated semiconductor device according to any one of Claims 4 to 6, wherein the semiconductor device is a memory and the polyamide resin film has a thickness of 35–300 μm.

9. A resin encapsulated semiconductor device according to any one of Claims 1 to 8, wherein the insulator layer provided on the surface of the semiconductor element is a phosphilicate glass protective layer.

10. A resin encapsulated semiconductor device according to Claim 9, wherein the phosphorus concentration in the phosphosilicate glass is about 10% by mole or above.

11. A resin encapsulated semiconductor device substantially as hereinbefore described with particular reference to the drawings and the Examples.

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